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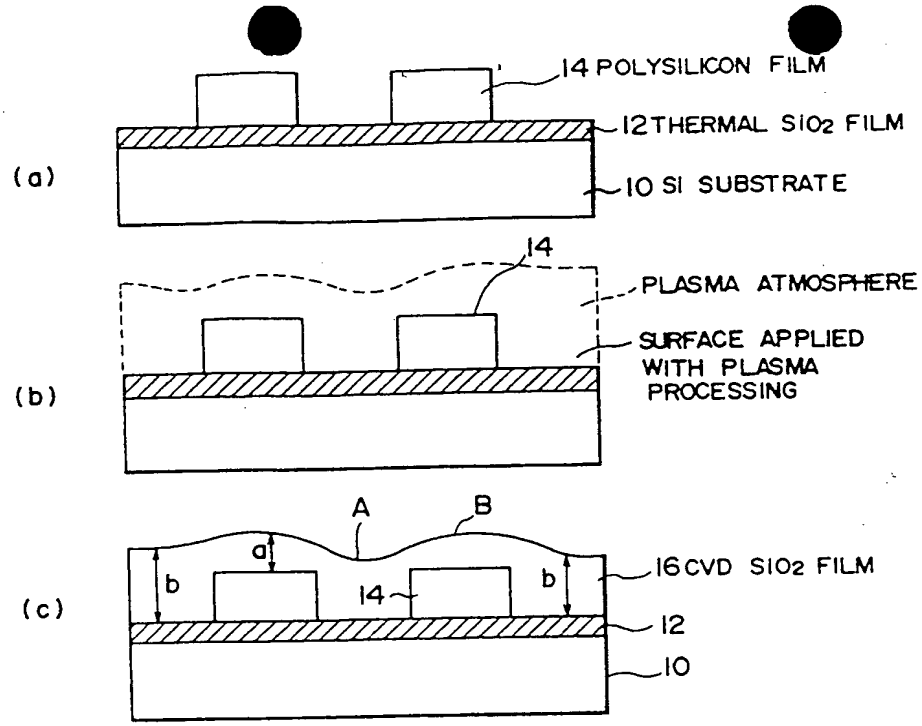
(54) Method of manufacturing a silicon oxide film and an oxide based glass for semiconductor devices.

(57) According to the present invention, there are provided a manufacturing method of a semiconductor device, characterized in that, after a surface of a substrate is reformed by performing high frequency plasma irradiation processing in a state that the substrate is heated, organic silane and ozone are mixed with each other, and a silicon oxide film is formed on the substrate under normal pressure or reduced pressure and also a manufacturing method of a semiconductor device, characterized in that, after a surface of a substrate is reformed by performing high frequency plasma irradiation processing in a state that the substrate is heated, organic silane, gas containing impurities such as phosphorus or boron and ozone are mixed, and a PSG film, a BSG film, a BPSG film and the like are formed on the substrate under normal pressure or reduced pressure.

EP 0 470 632 A2



EXPLANATORY VIEW OF MANUFACTUING METHOD OF SEMICONDUCTOR DEVICE ACCORDING TO EMBODIMENT OF THE PRESENT INVENTION

FIG. 1

BACKGROUND OF THE INVENTION

The present invention relates to a manufacturing method of a semiconductor device, and more particularly to a manufacturing method of a semiconductor device for forming a silicon oxide film and a PSG film, a BSG film, or a BPSG film and the like by mixing organic silane and ozone, or gas containing an impurity such as phosphorus and boron.

The inventors of the present application have already found that a SiO_2 film formed by a TEOS-O_3 reaction has such advantages that step coverage is excellent and that very few particles are generated during film formation, and have also found that characteristics of the film depend on the O_3 concentration, and the following characteristics are obtainable as the O_3 concentration gets higher.

① Increase of film forming speed
② Increase of film density
③ Reduction of etching rate
④ Reduction of leakage current
⑤ Reduction of -OH, H_2O components in a film
⑥ Improvement of crack resistance
⑦ Reduction of stress
⑧ Improvement of step coverage
(Flow configuration)

On the other hand, however, the TEOS-O_3 reaction being a surface reaction, the reaction is very sensitive to a substrate surface on which the film is accumulated, and the characteristics of formed films are different sometimes when substrate films are different.

Fig. 7 shows a forming method of a CVD-SiO_2 film by Tetra-Ethyl-Ortho-Silicate (TEOS , $Si(OC_2H_5)_4$)-O_3 reaction according to a conventional exemplification for explaining the foregoing.

In Fig. 7 (a), a reference numeral 4 denotes a thermal SiO_2 film formed on a surface of a Si substrate 2, and 6 denotes a polycrystalline silicon film (hereinafter referred to in brief as a "poly-Si film") formed on the thermal SiO_2 film 4. Examples of semiconductor devices having such a structure includes a MOS transistor comprising the thermal SiO_2 film 4 as a gate SiO_2 film and the poly-Si film 6 as a gate electrode for instance.

Next, a CVD-SiO_2 film 8 is formed as an interlayer insulating film by the TEOS-O_3 reaction as shown in Fig. 7 (b).

Hereupon, it has been found that the surface of the CVD-SiO_2 film 8 accumulated by the TEOS-O_3 reaction is even (see a partially enlarged view A) in case the backing is of the poly-Si film 6 as shown in a perspective view of Fig. 7 (c), but that unevenness is produced on the film surface sometimes (see a partially enlarged view B) in case the backing is of the thermal SiO_2 film 4.

Fig. 8 is a diagram showing measurement results of unevenness on the surface of the CVD-SiO_2 film formed using such a conventional method by the present inventors. In Fig. 8, an axis of abscissas shows ozone concentration (%), an axis of ordinate shows the difference in unevenness on the surface of the CVD-SiO_2 film (Å), and parameters are backings (thermal SiO_2 film, Si film). In such a manner, an even CVD-SiO_2 film surface is obtainable regardless of the O_3 concentration in case the backing is of Si, but the film surface depends on the O_3 concentration when the backing is of the thermal SiO_2 film, and there is such a tendency that the unevenness on the CVD-SiO_2 film surface becomes more intense as the O_3 concentration gets higher.

Besides, the unevenness was measured by applying a probe to the surface of the accumulated SiO_2 film and measuring a distance of vertical movement thereof.

Next, Fig. 9 is a diagram showing the result of measurement of an accumulation rate of the CVD-SiO_2 film formed by using a conventional method same as that used in Fig. 8. As shown in the Figure, control is easy in point of manufacturing since dependency of the accumulation rate on the O_3 concentration is small when the O_3 concentration reaches approximately 1% and higher in case the backing is of Si, but the accumulation rate depends greatly on the O_3 concentration when the backing is of a SiO_2 film, and the accumulation rate is lowered as the O_3 concentration gets higher. Thus, there is such a problem that difficulty in manufacturing such as control of a film thickness is found.

Then, when the O_3 concentration is lowered (approximately 3% and lower), the film quality of the CVD-SiO_2 film is not sufficient, and the step coverage at a step portion changes from a flow configuration to an isotropy, which, therefore, shows a difficult point when the CVD-SiO_2 film is used as an interlayer insulating film.

As described, a conventional method has such a dilemma therewithin that the film quality is good but subject to a serious influence of the backing when the O_3 concentration is high. On the other hand,

however, the film quality is difficult to be affected by the backing but the film quality is deteriorated when the O_3 concentration is low. Thus, it is difficult to solve all the problems at the same time by setting a specific O_3 concentration.

It is an object of the present invention which has been made in view of the problems in such a conventional exemplification to provide a manufacturing method of a semiconductor device characterized in that a CVD film such as a SiO_2 film and a BPSG film in which generation of unevenness on the film surface is controlled and a CVD film such as a SiO_2 film and a BPSG film which has a stabilized accumulation rate, is suitable for flattening, and has a good film quality is formed.

A manufacturing method of a semiconductor device of the present invention is characterized in that, after applying high frequency plasma irradiation processing to a surface of a substrate while heating the same so as to reform the substrate surface, organic silane and ozone are mixed with each other and a silicon oxide film and a like are formed on the substrate under atmospheric pressure or reduced pressure.

When the inventors of the present application has perceived the fact that the characteristic of an accumulated film depends on a surface state of a substrate since the organic silane (such as TEOS)-O_3 reaction is a surface reaction, and have tried various methods as surface processing, it was found that plasma processing was the best.

For example, when organic silane (TEOS) and ozone O_3 are mixed with each other and a silicon oxide film (CVD-SiO_2 film 16) is formed on a substrate under atmospheric pressure or reduced pressure after reforming the surface of the substrate (thermal SiO_2 film 12) (Fig. 1 (b)) by applying high frequency plasma irradiation processing in a state that the substrate (a Si substrate 10) is heated as illustrated in Fig. 1, a film thickness b of a SiO_2 film accumulated on the thermal SiO_2 film 12 becomes equal to a film thickness a of a SiO_2 film accumulated on the poly-Si film 12 ($a = b$), and the unevenness on the surface also disappears, thus solving the conventional problems.

This phenomenon is conjectured to have occurred due to the fact that the surface of the thermal SiO_2 film 12 has been reformed from a hydrophilic property to a hydrophobic property by plasma irradiation processing.

Fig. 2 shows this phenomenon schematically. Namely, the surface of the thermal SiO_2 film has a hydrophilic property before plasma processing because of existence of -OH radical, but it is conjectured that the surface has been reformed as shown in the Figure because of the fact that the Si-OH coupling is broken by means of plasma processing. It can be confirmed practically that a hydrophilic property has been changed to a hydrophobic property by measuring and comparing a contact angle of water at the surface of the thermal SiO_2 film before and after plasma processing.

Besides, a high frequency used in plasma processing is at 13.56 MHz in general, but may be at 100 to 200 KHz. However, since surface reformation is the object, it is required to set the amplitude of electric power to such an extent that is not attended with film formation and etching of the substrate.

Further, activating gas of Ar or He system, N_2 or $O_2$is appropriate for the use gas.

Furthermore, the present invention is applicable not only to a case in which the combination of the backing illustrated in Fig. 1 is a poly-Si film, but also to cases of the following combinations of the backing.

Al-BPSG, PSG, thermal SiO_2
W-BPSG, PSG, thermal SiO_2
WSi_x-BPSG, PSG, thermal SiO_2
Al-BPSG, PSG, thermal SiO_2
Poly-Si-BPSG, PSG, thermal SiO_2

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows explanatory drawings of a manufacturing method of a semiconductor device according to an embodiment
of the present invention; Fig. 2 is a diagram for explaining the operation of the present invention;
Fig. 3 shows schematic block diagrams of plasma surface processing apparatus according to embodiments of the present invention;
Fig. 4 is a schematic block diagram of a CVD film forming apparatus according to an embodiment of the present invention;
Fig. 5 is a diagram for explaining an accumulation rate of a CVD-SiO_2 film according to a manufacturing method of the present invention;
Fig. 6 is a diagram for explaining a surface state of a CVD-SiO_2 film according to a manufacturing method of the present invention;
Fig. 7 shows explanatory drawings of a conventional manufacturing method;

Fig. 8 is a diagram for explaining a surface state of a CVD-SiO_2 film according to a conventional manufacturing method; and
Fig. 9 is a diagram for explaining an accumulation rate of a CVD-SiO_2 film according to a conventional manufacturing method of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the next place, embodiments and experimental examples of the present invention will be described with reference to the drawings.

(1) Description of an embodiment of the present invention

① The first process

Fig. 1 shows drawings for explaining a forming method of a SiO_2 film by a CVD method of the TEOS-O_3 reaction according to an embodiment of the present invention, in which a numeral 12 denotes a thermal SiO_2 film formed on a surface of a Si substrate 10 by means of thermal processing, and 14 denotes a poly-Si film formed on above-mentioned thermal SiO_2 film 12. For example, a MOS transistor including a thermal SiO_2 film 12 as a gate SiO_2 film and a poly-Si film 14 as a gate electrode has such a structure as described above.

② The second process

Next, when the Si substrate 10 is placed in a plasma surface processing apparatus shown in Fig. 3 (a) and exposed in a plasma atmosphere of N_2 gas, the Si-OH coupling on the surface of the thermal SiO_2 film 12 is broken and the surface is reformed (see Fig. 1 (b)) as shown in a schematic diagram of Fig. 2.

An RF plasma apparatus of a parallel plate anode coupling system shown in Fig. 3 (a) for instance is used for the plasma processing.

In Fig. 3 (a), 18 denotes a chamber, 20 denotes an upper electrode supplied with high frequency electric power from an RF power source 22, and 24 denotes a heater which heats a wafer 26.

When plasma processing is performed, the wafer 26 is placed on a susceptor (heater 24) in the chamber 18 and heated to approximately 350° for instance, and then N_2 gas is introduced therein, and high frequency electric power at 200 W and 13.56 MHz is applied to the upper electrode 20, thereby to bring N_2 gas into a plasma state. Approximately one minute will suffice for the processing time at that time.

Besides, a batch type RF plasma processing apparatus having a coil for discharging in a tubular furnace as shown in Fig. 3 (b) may be used as the plasma processing apparatus.

In Fig. 3 (b), 28 denotes a chamber, 30 denotes a heater, 32 denotes an RF power source, 34 denotes discharge electrode plates, and 36 denotes a wafer which is an object to be processed.

③ The third process

Next, a CVD-SiO_2 film by the TEOS-O_3 reaction is accumulated on a surface of a substrate reformed by plasma processing in the second process as shown in Fig. 1 (c). For example, the temperature of the substrate is set to 400° C, the TEOS source temperature is set to 65° C (saturated vapor pressure at 20 mmHg), the O_3 concentration is set to 5%, the flow rate of the carrier gas N_2 is set to 3.5 SLM and processing is performed for 7 to 8 minutes using a CVD film forming apparatus shown in Fig. 4.

With this, a SiO_2 film having the film thickness of approximately 1 μm is accumulated, but the film thickness b of the CVD-SiO_2 film formed on the thermal SiO_2 film 12 and the film thickness a of the CVD-SiO_2 film formed on the poly-Si film 14 becomes equal to each other (a = b) at that time, and the unevenness on a surface A of a CVD-SiO_2 film on the thermal SiO_2 film 12 disappears similarly to a surface B of the CVD-SiO_2 film on the poly-Si film 14, and the surface A becomes very smooth. Further, coverage of above-mentioned CVD-SiO_2 film with respect to steps on the poly-Si film was also excellent.

(2) Extended example and experimental example of the embodiment of the present invention

① Another embodiment of the present invention

Fig. 4 is a schematic block diagram of a CVD film forming apparatus used in a manufacturing method

according to an embodiment of the present invention. In Fig. 4, 38a to 38d denote flowmeters (MFC), 40a to 40h denote valves, 42 denotes an ozonizer which changes oxygen (O_2) into ozone (O_3), 44 denotes a TEOS solution which is set at a temperature of 40 to 65° C, 46 denotes a tri-metyl phosphate (TMPO) solution which is set at 50 to 60° C, and 48 denotes a tri-etyl borate (TEB) solution which is set at 5 to 50° C.

Further, 50 denotes a chamber, 52 denotes a heater, 54 denotes a head for effluence of gas, 56 denotes a gas exhaust port, and 58a and 58b denote wafers which become objects of film formation.

When a SiO_2 film is accumulated, the valves 40a to 40d are opened in the manufacturing apparatus shown in Fig. 4. With this, O_3 gas coming out of the ozonizer 42 and TEOS gas sent out through carrier gas N_2 are supplied into the chamber 50 from the head 54 for effluence of gas, the TEOS gas is decomposed by O_3 on the wafers 58a and 58b, and a CVD-SiO_2 film is accumulated on the surfaces of the wafers.

Besides, the O_3 concentration is changed by adjusting O_2 - O_3 transformation quantity in the ozonizer 42 or by regulating a flowmeter MFC 38a and a valve 40a or 40b.

Further, when a PSG film, a BSG film or a BPSG film and the like are accumulated other than the SiO_2 film, they may be formed selectively by opening and closing the valves 40a to 40h appropriately.

Furthermore, a CVD film by the TEOS-O_3 reaction has been described in the embodiment, but the present invention is also applicable to a film formed by the reaction between other alkoxysilane and various siloxane compound (for example, polysiloxane (Octe-Methyl-Cyclo-Tetra-Siloxiane) and the like) and O_3.

② Experimental example of the present invention (1)

Fig. 5 is a diagram showing an accumulation rate when a SiO_2 film by the TEOS-O_3 reaction is accumulated on a Si substrate having a hydrophobic surface and an accumulation rate when a SiO_2 film by the TEOS-O_3 reaction is accumulated after the thermal SiO_2 film on a hydrophilic surface is reformed into a hydrophobic surface through plasma processing. The axis of abscissas shows the O_3 concentration, the axis of ordinate shows an accumulation rate, and accumulating conditions are such that the substrate temperature is at 400° C and the TEOS source temperature is at 65° C.

As shown in the Figure, the accumulation rate of the SiO_2 film on the thermal SiO_2 film becomes almost equal to the accumulation rate of the SiO_2 film on the Si substrate regardless of the O_3 concentration, thus making it possible to solve conventional problems (on the contrary, according to a conventional method in which plasma processing is not performed, the accumulation rate of the CVD-SiO_2 film on the thermal SiO_2 film shows a bigger difference from the accumulation rate of the CVD-SiO_2 film on the poly-Si film as the O_3 concentration gets higher (see Fig. 8).

③ Experimental example of the present invention (2)

Further, Fig. 6 is a diagram showing the result of measurement of the unevenness on the surface of a SiO_2 film when the SiO_2 film by the TEOS-O_3 reaction is accumulated on a Si substrate having a hydrophobic surface and the unevenness on a surface of a SiO_2 film when the SiO_2 film by the TEOS-O_3 reaction is accumulated after the thermal SiO_2 film having a hydrophilic surface is reformed into a hydrophobic surface through plasma processing. The axis of abscissas shows the O_3 concentration, the axis of ordinate shows the accumulation rate, and the accumulation conditions are such that the substrate temperature is at 400° C and the TEOS source temperature is at 65° C.

As shown in Fig. 6, unevenness does not appear on the surface of the SiO_2 film of the CVD-SiO_2 film accumulated on the thermal SiO_2 film after plasma processing even when the O_3 concentration gets high. Naturally, unevenness does neither appear regardless of the O_3 concentration on the surface of the CVD-SiO_2 film accumulated on the poly-Si film (on the contrary, with a conventional method in which plasma processing is not performed, the unevenness on the surface of the CVD-SiO_2 film on the thermal SiO_2 film becomes more intense as the O_3 concentration is increased (see Fig. 9).

As described above, according to the embodiment of the present invention, it is possible to form a film having the same film thickness and no unevenness on the surface while obtaining a SiO_2 film of high quality by the TEOS-high concentration O_3 reaction and eliminating the influence by a backing film for accumulation by such a simple method that plasma processing is performed before a CVD-SiO_2 film is accumulated by a reaction containing organic silane and O_3 thereby to reform the surface of the substrate. Hence, the embodiment is very effectual when it is applied to formation of an interlayer insulating film of a semiconductor device such as a VLSI.

④ Experimental example of the present invention (3)

Table 1 shows the effect of a plasma processing method according to an embodiment of the present invention. The plasma processing conditions are such that processing has been performed under N_2 gas, a high frequency power source at 13.56 MHz, electric power at 200 W and a degree of vacuum at 1 Torr, and accumulation conditions of the CVD-SiO_2 film are such that accumulation has been performed under the substrate temperature at 400° C and the O_3 concentration at 5%.

The criterion of the effects has been judged by the magnitude of the difference between the accumulation rate of the CVD-SiO_2 film accumulated on the thermal SiO_2 film and the accumulation rate of the CVD-SiO_2 film accumulated on Si, and the intensity of the unevenness on the surface of the CVD-SiO_2 film. In the table, a mark o shows effectual, a mark Δ shows effectual to some extent, and a mark x shows non-effectual.

TABLE 1

Substrate Temperature (°C)	Processing Time (minutes)				
	1 min.	5 min.	10 min.	30 min.	60 min.
Room Temperature	x	x	x	x	x
100°C	x	x	x	x	x
150°C	x	x	x	Δ	Δ
200°C	x	x	Δ	Δ	o
250°C	Δ	Δ	o	o	o
300°C	o	o	o	o	o
350°C	o	o	o	o	o
400°C	o	o	o	o	o

It is realized through the experimental results that it is possible to reform the surface with processing in N_2 gas for approximately one minute when the substrate temperature is set at 350° C.

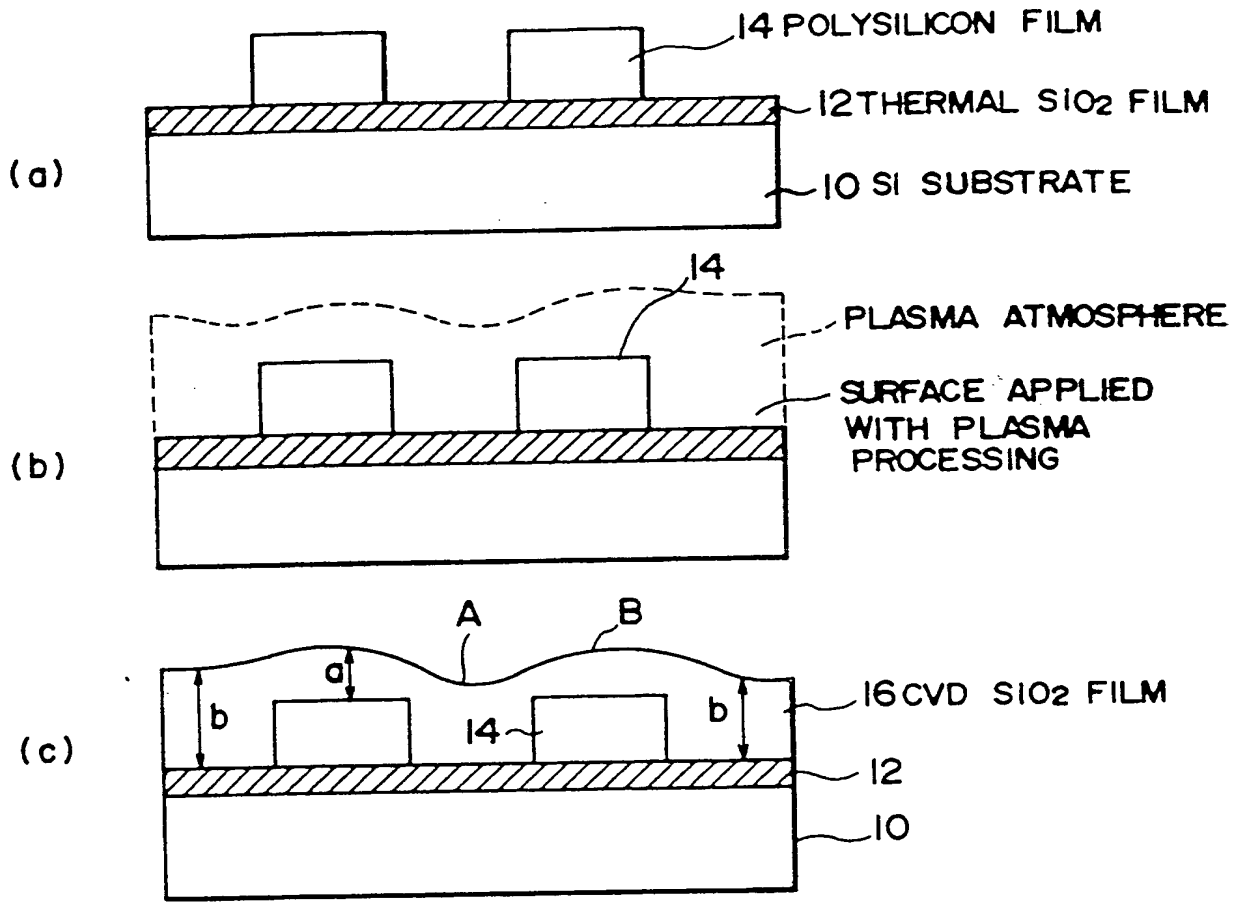
As described above, according to a manufacturing method of the present invention, it is possible to form a film having even film thickness and no unevenness on the surface on a backing film while obtaining a film of high quality by high concentration O_3 reaction and eliminating the influence of the backing film by such a simple method that plasma processing is performed before a CVD-SiO_2 film is accumulated by a reaction containing organic silane and O_3 thereby to reform the surface of the substrate. Accordingly, the present invention is very effectual when it is applied to formation of an interlayer insulating film of a semiconductor device such as a VLSI in submicron having a multi-layer structure.

Claims

1. A manufacturing method of a semiconductor device, characterized in that, after a surface of a substrate is reformed by performing high frequency plasma irradiation processing in a state that the substrate is heated, organic silane and ozone are mixed with each other, and a silicon oxide film is formed on said substrate under normal pressure or reduced pressure.

2. A manufacturing method of a semiconductor device, characterized in that, after a surface of a substrate is reformed by performing high frequency plasma irradiation processing in a state that the substrate is

heated, organic silane, gas containing impurities such as phosphorus or boron and ozone are mixed, and a PSG film, a BSG film, a BPSG film and the like are formed on said substrate under normal pressure or reduced pressure.



EXPLANATORY VIEW OF MANUFACTUING METHOD OF SEMICONDUCTOR DEVICE ACCORDING TO EMBODIMENT OF THE PRESENT INVENTION

FIG. 1

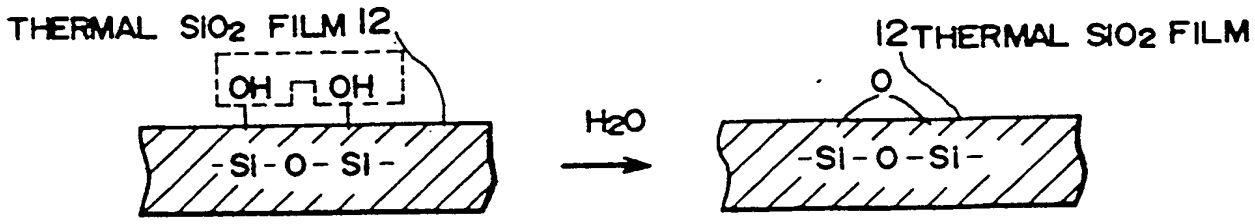
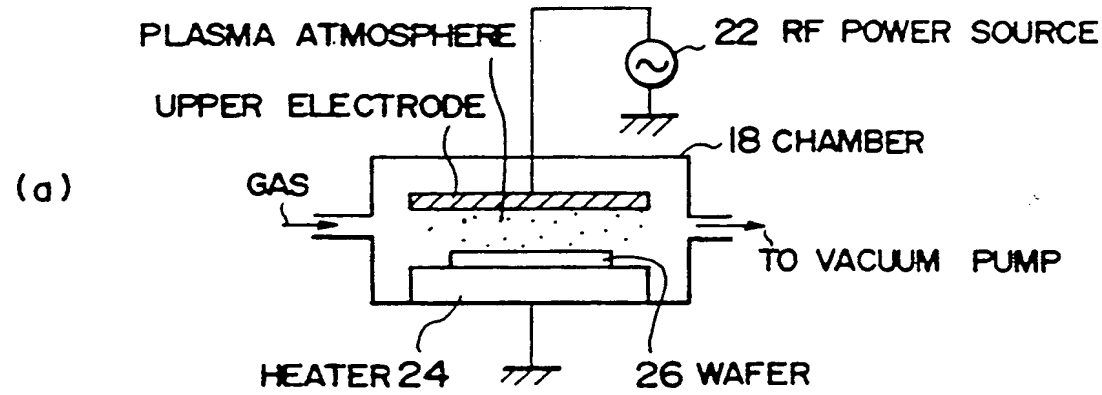
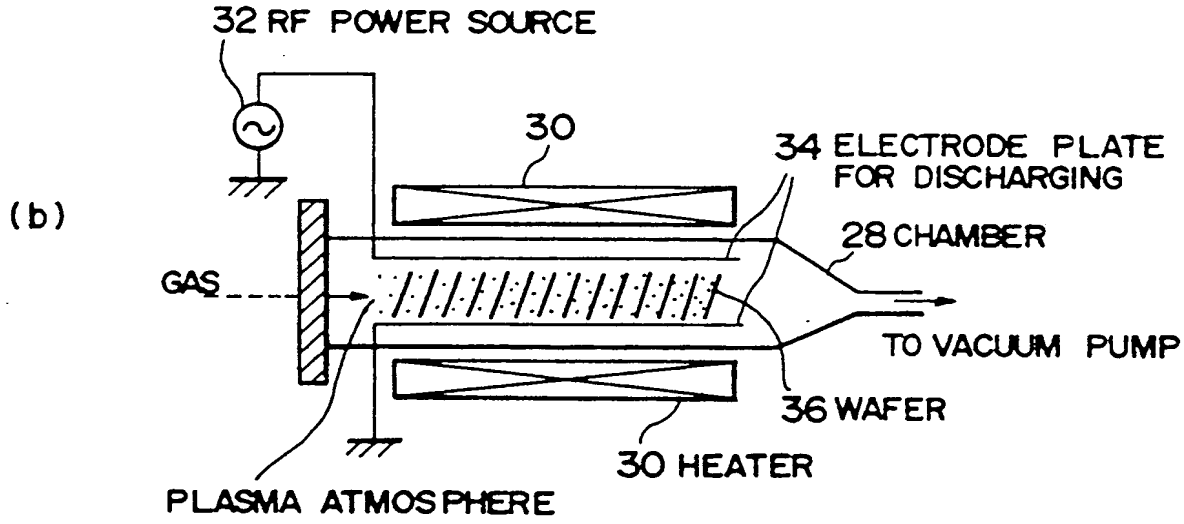


DIAGRAM FOR EXPLAINING OPERATION OF THE PRESENT INVENTION SCHEMATICALY

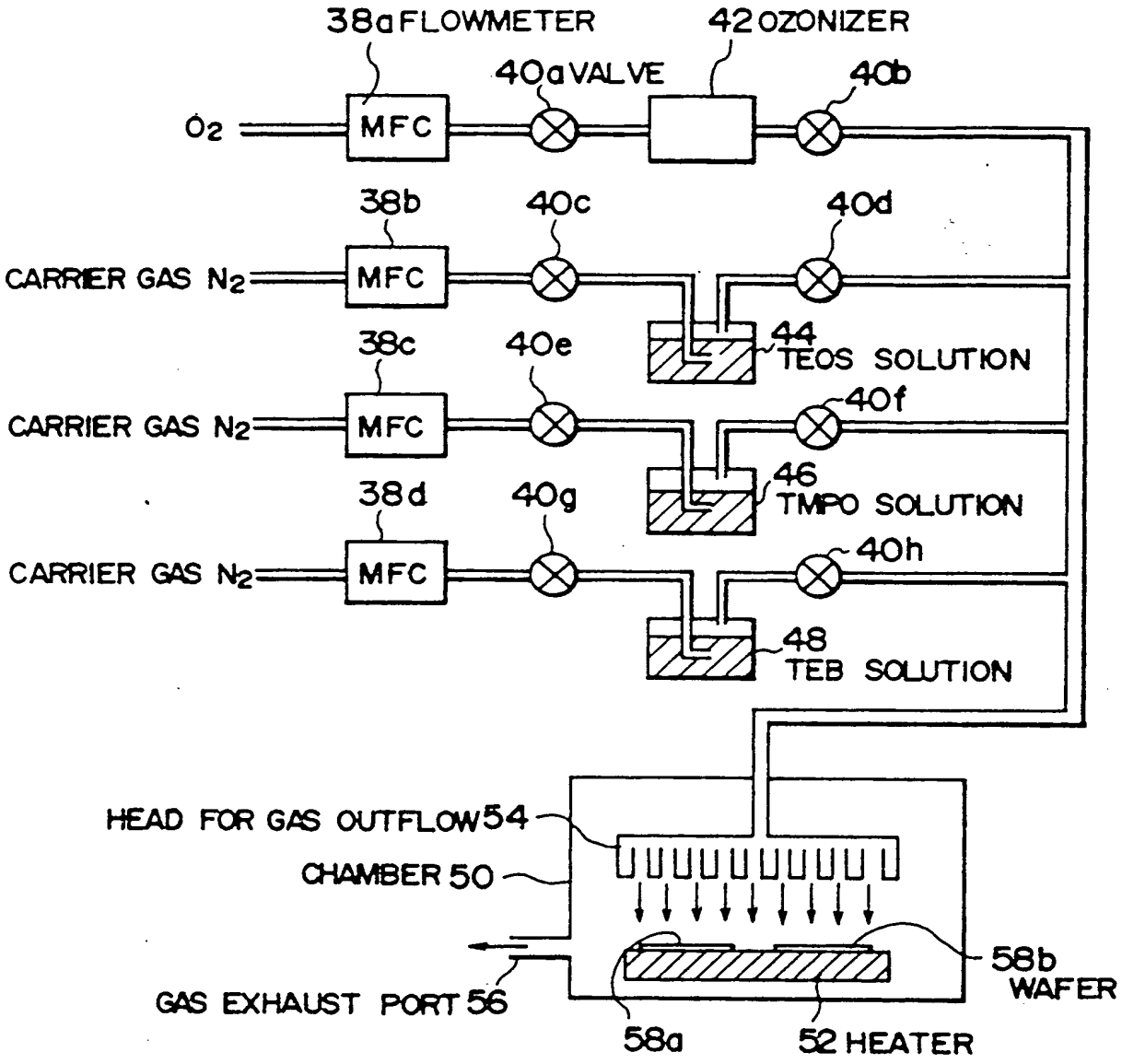
FIG. 2





SCHEMATIC BLOCK DIAGRAM OF PLASMA SURFACE PROCESSING APPARATUS ACCORDING TO EMBODIMENT OF THE PRESENT INVENTION

FIG. 3



SCHEMATIC BLOCK DIAGRAM OF CVD FILM FORMING APPARATUS ACCORDING TO EMBODIMENT OF THE PRESENT INVENTION

FIG. 4

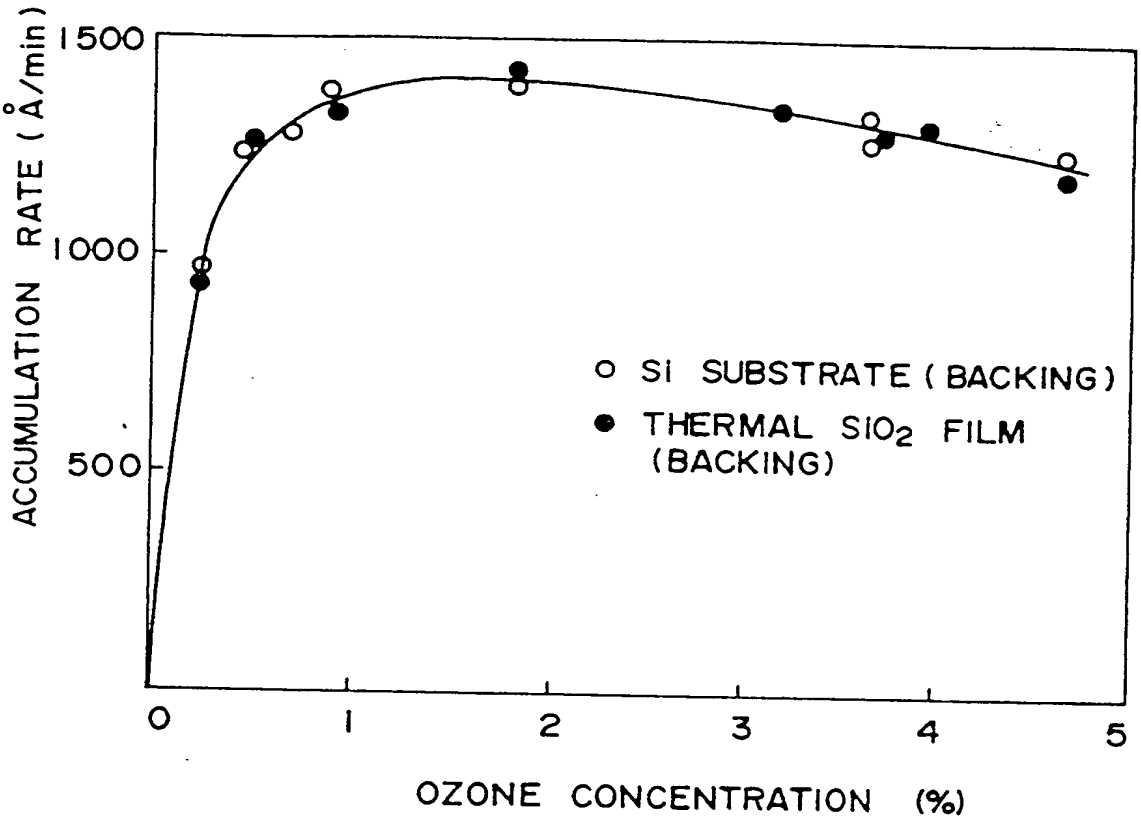


DIAGRAM FOR EXPLAINING ACCUMULATION RATE OF CVD-SiO_2 FILM ACCORDING TO MANUFACTURING METHOD OF THE PRESENT INVENTION

FIG. 5

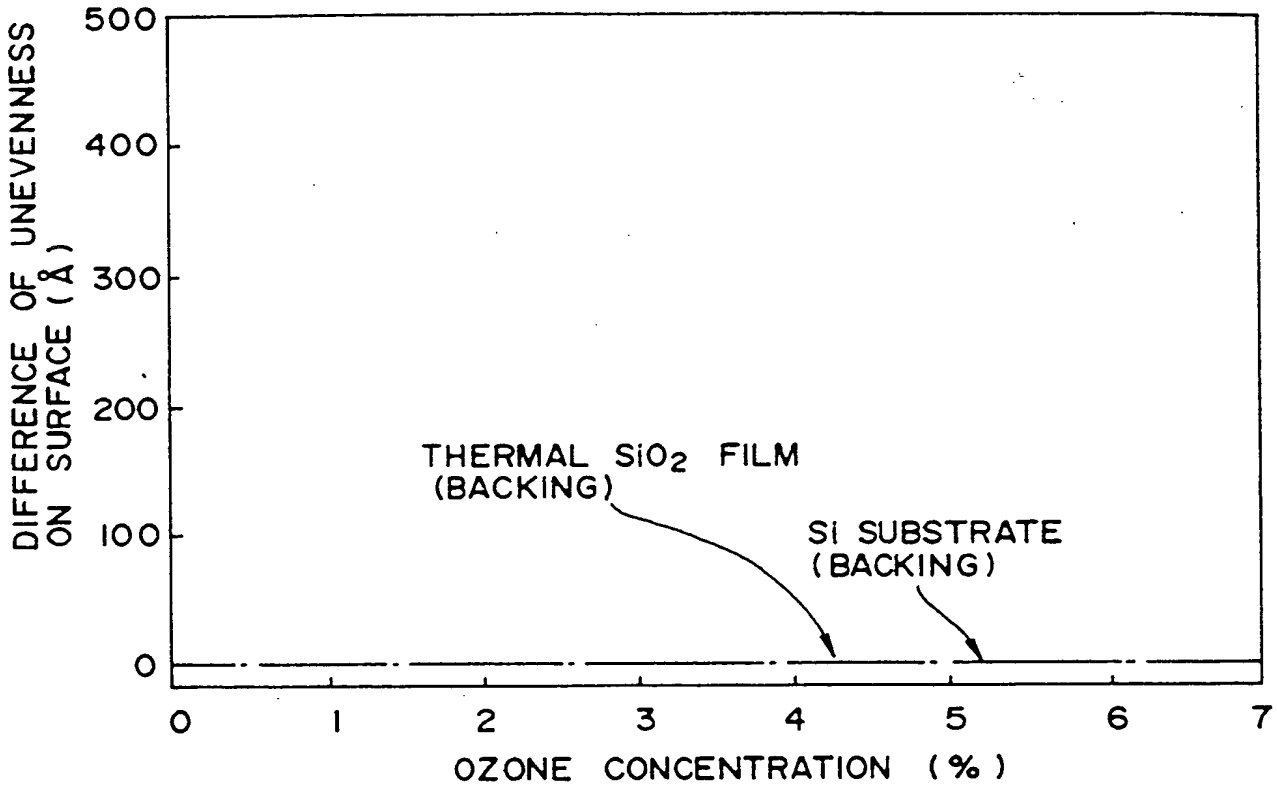
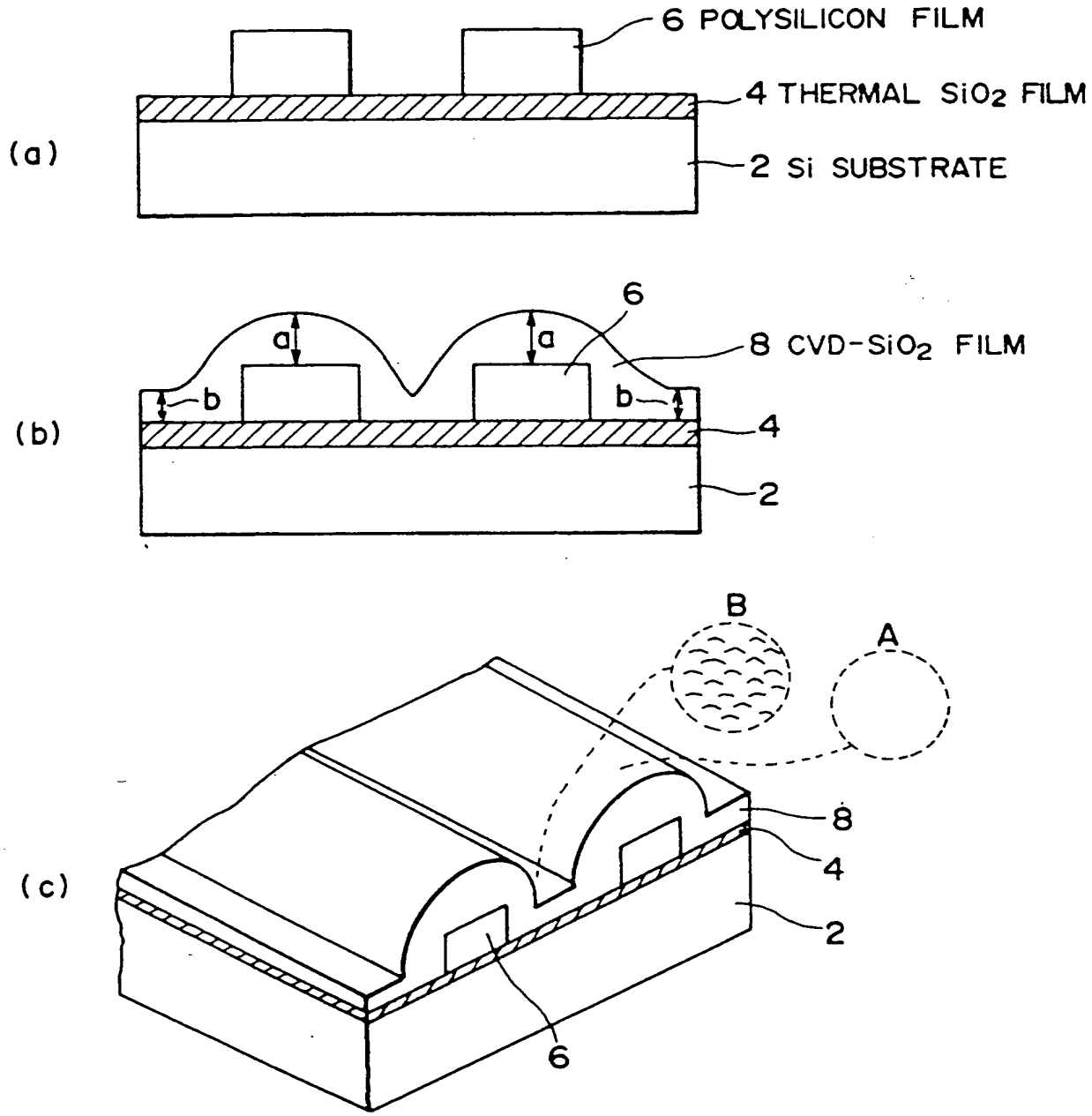


DIAGRAM FOR EXPLAINING SURFACE STATE OF CVD-SiO_2 FILM ACCORDING TO MANUFACTURING METHOD OF THE PRESENT INVENTION

FIG. 6



EXPLANATORY VIEW OF CONVENTIONAL MANUFACTURING METHOD

FIG. 7

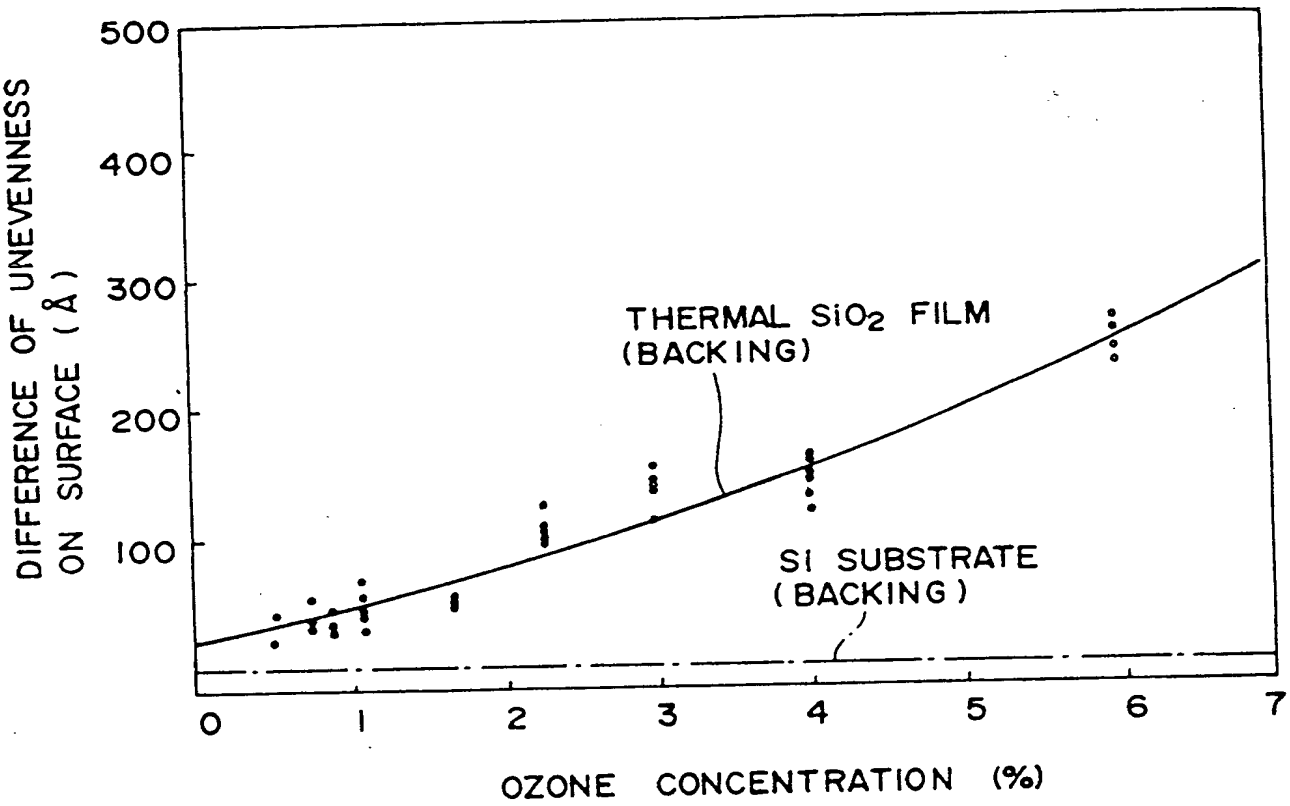


DIAGRAM FOR EXPLAINING SURFACE STATE OF CVD SiO_2-FILM ACCORDING TO CONVENTIONAL MANUFACTURING METHOD

FIG. 8

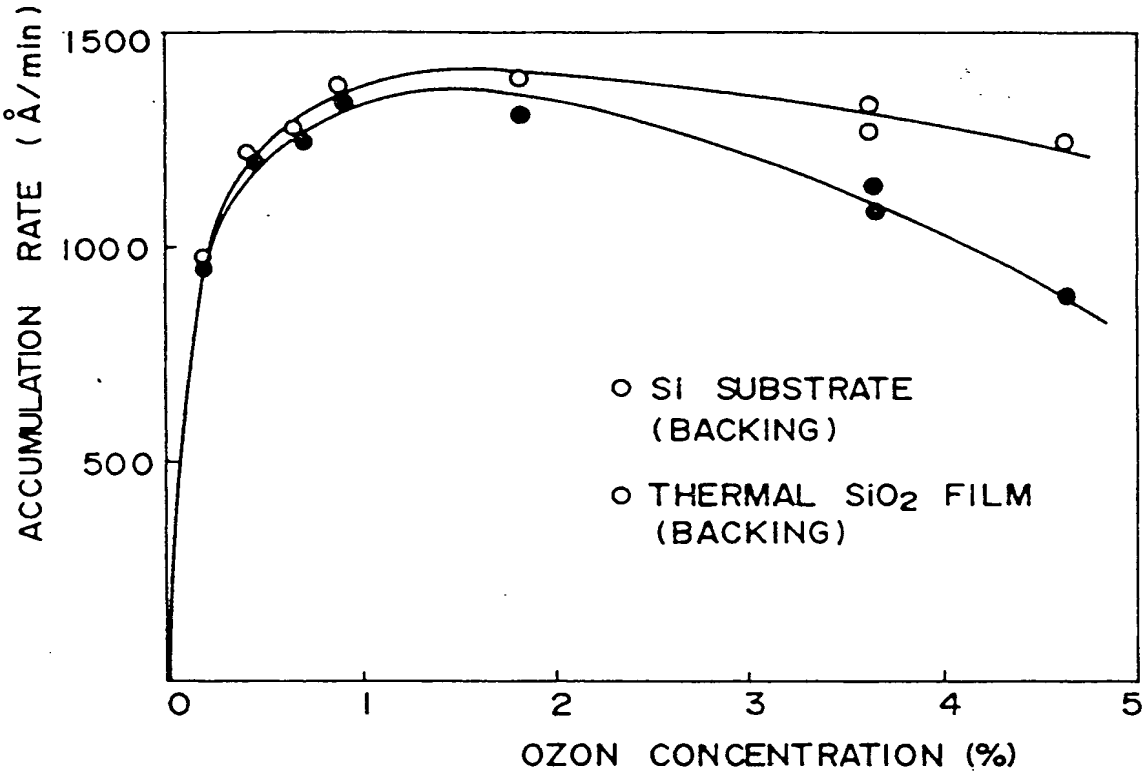


DIAGRAM FOR EXPLAINING ACCUMULATION RATE OF CVD-SiO_2 FILM ACCORDING TO CONVENTIONAL MANUFACTURING METHOD

FIG. 9